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MAGNESIUM-ETHOXIDE-BASED TITANIUM CATALYSTS FOR POLYMERIZATION OF PROPYLENE

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ABSTRACT

Supported titanium catalysts are prepared by the reactions of magnesium ethoxide and excess titanium tetrachloride with or without an internal Lewis base, dibutyl phthalate. The catalysts are characterized by compositional analysis and BET surface area measurements. The performance of catalysts using triethylaluminum and dimethoxydiphenylsilane as the cocatalyst system are examined for propylene polymerization in slurry reactions. The dibutyl phthalate and phenyl-substituted methoxysilane used as internal and external Lewis bases, respectively, govern the activity and stereospecificity of the catalyst system. Such polymerization parameters as time, temperature, and hydrogen concentration also influence the performance of the catalytic system in terms of yield, isotactic index, and melt flow index of the polypropylene.

INTRODUCTION

Supported titanium catalysts, categorized as third generation Ziegler-Natta systems, show high activity and stereospecificity for the polymerization of propylene [1–3]. Inorganic support of magnesium compounds such as MgO, Mg(OH)₂, MgCO₃, and MgCl₂ are used for the incorporation of titanium tetrachloride [4, 5]. Among these compounds, magnesium dichloride is preferred due to its layered lattice structure (similar to that of titanium trichloride crystals), facile complexation

behavior, and other physical characteristics [6]. A number of methodologies are employed for the preparation of catalysts using anhydrous magnesium dichloride as the starting material. These catalysts have been extensively investigated for their physicochemical properties and polymerization behavior [7–15].

A prerequisite for high activity of magnesium-dichloride-supported titanium catalysts is the conversion of crystalline α - MgCl_2 to the δ -form. This is achieved either by ball milling [2, 3] or by controlled generation of MgCl_2 from its alcohol adduct [15, 16]. Difficulties are also encountered in handling MgCl_2 due to its hygroscopic nature [17]. Such factors have led to searches for the in-situ generation of MgCl_2 using organomagnesium compounds. Mg-O bonded compounds are expected to generate highly distorted magnesium dichloride crystallites through an exchange reaction with M-Cl bonded species. The patent literature [18] indicates that magnesium-alkoxide-based titanium catalysts are highly active and stereospecific for propylene polymerization. Internal Lewis bases, such as monoesters and diesters, are incorporated in the solid catalysts. However, the published information [19–22] deals with catalysts prepared by using the monoester-like ethylbenzoate. The activity of such catalysts is higher than that of corresponding catalysts prepared with anhydrous magnesium dichloride [23] as the starting material.

The present study discusses the preparation, characterization, and performance aspects of magnesium-ethoxide-based titanium catalysts containing dibutyl phthalate as an internal Lewis base. Different types of phenyl-substituted methoxy-silane are used as an external Lewis base in order to study their influence on the productivity of the catalysts. The effects of polymerization parameters on the activity and stereospecificity of catalyst systems are also described.

EXPERIMENTAL

Materials

Magnesium ethoxide (Hüls, Germany) and triethylaluminum (Ethyl Corporation, USA) were commercially obtained and used without further purification. Titanium tetrachloride, dibutyl phthalate, trimethoxyphenylsilane, dimethoxydiphenylsilane and methoxytriphenylsilane were used after distillation. Decane, hexane, and chlorobenzene were dried over sodium wire and distilled before use. Ultrapure hydrogen gas and propylene (from a commercial PP plant) were used without further purification.

Procedures

All experimental manipulations were carried out under a high purity nitrogen atmosphere. Standard Schlenk techniques and a Vacuum Atmospheres Model HE-43 Dri-Lab equipped with a model HE 491 Dri Train were used for handling all compounds.

Catalyst Preparation

Catalysts MgTi-A, B, and C were prepared by heating mixtures of $\text{Mg}(\text{OEt})_2$ (7.7 g), TiCl_4 /chlorobenzene (100 mL; 1:1 v/v), and dibutyl phthalate (DBPh) at

120°C. The mole ratios of DBPh/Mg were: MgTi-A, DBPh/Mg = 0.0; MgTi-B, DBPh/Mg = 0.17; MgTi-C, DBPh/Mg = 0.30. After 2 hours the solid was allowed to settle and the liquid was siphoned off. The solid was again treated with 100 mL TiCl_4 at 120°C for 2 hours. The solid product was subsequently separated by decantation and washed with decane and hexane. The solid product thus obtained was kept in hexane.

Polymerization

In a 2.5-L stainless steel autoclave equipped with a stirrer, 900 mL hexane was first added under nitrogen atmosphere followed by a hexane solution of triethylaluminum, external Lewis base, and titanium catalyst. A known volume of hydrogen gas was introduced, and the propylene pressure and reaction temperature were raised to the required values. At the desired temperature, the total pressure was kept constant at $7.0 \pm 0.1 \text{ kg/cm}^2$ throughout the polymerization reaction. After completion of the reaction, the polymer product was separated, washed, and dried under vacuum at 60°C.

Characterization

Magnesium and chlorine contents of catalysts were estimated titrimetrically [24]. Titanium was analyzed quantitatively by the spectrophotometric method [24]. Solid samples were hydrolyzed in the acidic solution for quantitative estimation of dibutyl phthalate and ethoxy content as ethanol by gas chromatographic analysis [17, 18, 25]. BET surface areas of solid samples were measured on a Carlo-Erba Sorptomatic 1900 model. The polypropylene samples were extracted with boiling heptane in a Soxhlet apparatus. The isotactic index reported for each sample is the weight percentage of heptane-insoluble polypropylene. A Waters high temperature GPC instrument (model 150 C) was used for the determination of molecular weight of polypropylene samples at 145°C in trichlorobenzene. Ceast Instrument 6542 was used for measuring the melt flow index (MFI) at 2.16 kg and 230°C. The morphology of the polypropylene particles was studied by scanning electron microscopy (Model JEOL SEM 35 C).

RESULTS AND DISCUSSION

Catalysts Preparation

Magnesium ethoxide was used as a precursor for the generation of the active support. The support obtained was utilized for the incorporation of titanium tetrachloride with or without internal Lewis base dibutyl phthalate.

Magnesium-Ethoxide-Based Titanium Catalyst without Internal Lewis Base

Magnesium ethoxide was reacted twice with an excess amount of titanium tetrachloride. The solid product (MgTi-A) was isolated and characterized by compositional analysis (Table 1). The results [17, 19, 20] indicate the replacement of an

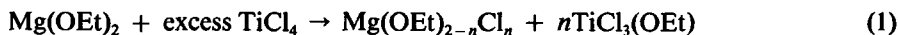
TABLE 1. Characteristics of Supported Titanium Catalysts

	Mg (OEt) ₂	MgTi-A	MgTi-B	MgTi-C
Mg ^a	21	11.8	17.2	15.0
Cl ^a	—	50.1	62.5	58.1
Ti ^a	—	13.0	4.0	3.0
Ethoxy ^a	78	8.4	<1	<1
Dibutyl phthalate ^a	—	—	14	23
Surface area (m ² /g)	20	124	207	182
Pore volume (cm ³ /g)	0.05	0.17	0.30	0.24
Polymerization activity ^b (kg PP/g catalyst)	—	1.7	6.6	4.3
Isotactic index (%)	—	70	96	98

^aWeight fraction in percent.

^bPolymerization conditions: $Pc_1^1 = 7.0 \pm 0.1$ kg/cm², $H_2 = 150 \pm 10$ mL, $Et_3Al = 5$ mmol, $Ph_2Si(OMe)_2 = 0.25$ mmol, time = 2 hours, catalyst = 30 ± 2 mg, 70°C.

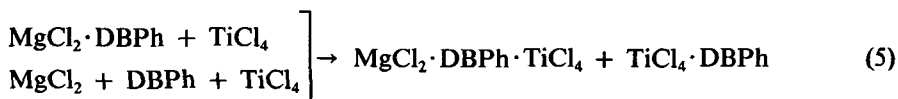
ethoxy group by chlorine in Mg(OEt)₂ generating a chlorinated support and TiCl₃(OEt) (Eqs. 1 and 2). At the same time, newly generated magnesium dichloride reacted with titanium compounds to produce the supported titanium catalyst (Eq. 3).

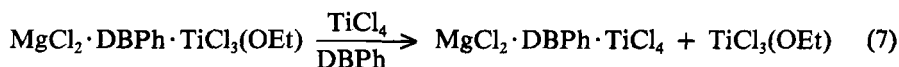
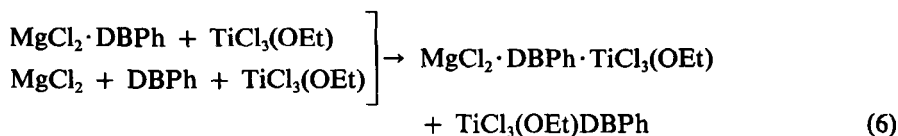


The reactions are nonstoichiometric.

Magnesium-Ethoxide-Based Titanium Catalyst with Internal Lewis Base

The reaction of magnesium ethoxide was carried out with titanium tetrachloride and dibutyl phthalate at different DBPh/Mg mole ratios. The solid obtained was further treated with excess titanium tetrachloride to isolate the catalyst (MgTi-B, DBPh/Mg = 0.17; MgTi-C, DBPh/Mg = 0.30). A sequence of reactions occurs [15, 16, 20, 21, 25] simultaneously in the reaction mixture to yield solid catalyst (Eqs. 1–7). It involves the chlorination of magnesium ethoxide (Eqs. 1 and 2), the formation of magnesium dichloride adduct with dibutyl phthalate (Eq. 4), and incorporation of titanium tetrachloride and titanium trichloroethoxide on the active support (Eqs. 5 and 6). Titanium trichloroethoxide incorporated on the support is easily knocked off [25] in the presence of titanium tetrachloride and dibutyl phthalate (Eq. 7).





The reactions are nonstoichiometric.

Catalyst Characterization

Compositional analysis (Table 1) of the solid products (MgTi-A vs MgTi-B) indicates that the addition of internal Lewis base brings a significant reduction in the amount of titanium incorporated. It may be linked with the removal of titanium trichloroethoxide from the active support in the presence of dibutyl phthalate [25]. At a higher concentration (DBPh/Mg = 0.30), the amount of dibutyl phthalate incorporated increases, resulting in a further reduction of titanium content (MgTi-C).

The changes in the specific surface area of magnesium ethoxide by chlorination with titanium tetrachloride are shown in Table 1. The two-time treatment of Mg(OEt)₂ with titanium tetrachloride increases the surface area from 20 to 124 m²/g. However, in the presence of dibutyl phthalate (DBPh/Mg = 0.17), the surface area for MgTi-B catalyst improves tenfold as compared to Mg(OEt)₂. A further increase of internal Lewis base concentration brings about a reduction in the surface area of the catalyst (MgTi-C). The fixation of about 3–4 wt% of titanium and the observation of 182–207 m²/g specific surface area of catalysts suggest a monolayer distribution of titanium tetrachloride on the support [21, 26].

Polymerization Study

Influence of Internal Lewis Base (dibutyl phthalate)

The productivity of the prepared catalysts were examined for the homopolymerization of propylene using triethylaluminum and dimethoxydiphenylsilane as the co-catalyst system. The data show (Table 1) that the activity of catalyst improves from 1.7 to 6.6 kg PP/g catalyst and the isotactic index increases from 70 to 96 wt% with the incorporation of dibutyl phthalate (MgTi-A vs MgTi-B). The enhancement in the activity is more than threefold compared to the catalyst without dibutyl phthalate (MgTi-A). A further increase in the amount of dibutyl phthalate (MgTi-C) reduces the polymer yield by approximately 34% with a marginal improvement in the isotactic index. In addition to the physical characteristics, the amount of TiCl₃(OEt) incorporated in the solid catalyst [25] and structural forms of titanium tetrachloride on the support (Fig. 1) [27, 28] may contribute toward variation in the performance of the catalyst system. According to Soga et al., the less active mononuclear titanium tetrachloride (Site A) and bi- or multinuclear titanium tetrachloride species may exist on the 100 cuts of the MgCl₂ support. The incorporation of internal Lewis base leads to the conversion of the titanium tetrachloride species of Site A into the highly active donor incorporated species (Site C). Furthermore, the addition of dibutyl phthalate reduces the amount of inactive TiCl₃(OEt) compound [25]. Thus, MgTi-B and

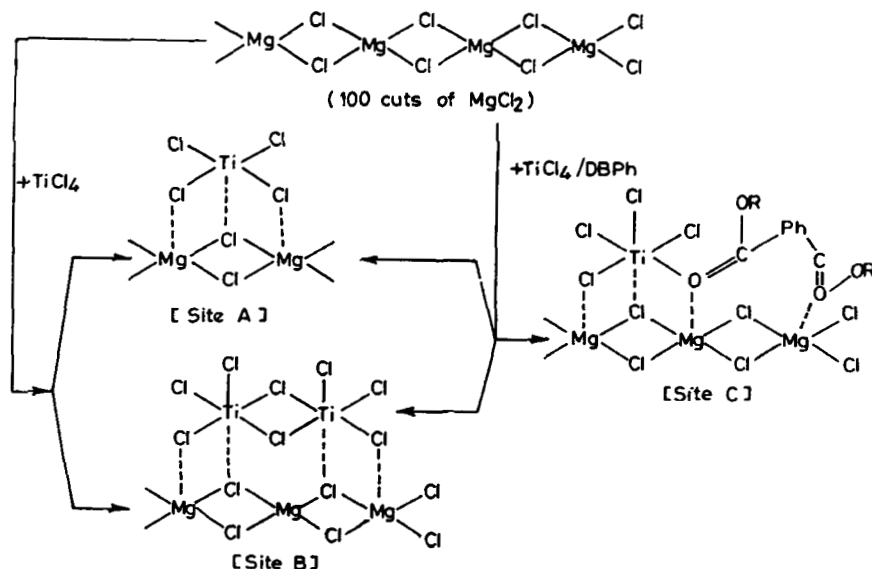


FIG. 1. Plausible titanium species on the 100 cuts of MgCl_2 with or without internal Lewis base.

MgTi-C catalysts with internal Lewis base incorporated show better performances compared to the Lewis-base-free MgTi-A catalyst.

Influence of External Lewis Base (phenyl-substituted methoxysilane)

The effect of phenyl-substituted methoxysilane, $\text{Ph}_n\text{Si}(\text{OMe})_{4-n}$ ($n = 1-3$), used in conjunction with triethylaluminum, was investigated by the performance of MgTi-B catalyst. The results show (Fig. 2) that there is no significant change in the yield and isotactic index of polypropylene by using either Et_3Al or the $\text{Et}_3\text{Al} + \text{Ph}_3\text{Si}(\text{OMe})$ cocatalyst systems. The use of $\text{Ph}_2\text{Si}(\text{OMe})_2$ significantly improves the isotactic index while reducing polymer yield. A further change to $\text{PhSi}(\text{OMe})_3$ shows a less pronounced effect on the isotactic index but decreases the polymer yield. The distribution of isotactic (heptane insoluble) and atactic (heptane soluble) contents of polypropylene are shown in Fig. 3. At a triethylaluminum-to-silane ratio of 20 the isotactic content reduces in the following order: $\text{Ph}_2\text{Si}(\text{OMe})_2 > \text{PhSi}(\text{OMe})_3 > \text{Ph}_3\text{Si}(\text{OMe})$ whereas the atactic polymer yield decreases in the order $\text{Ph}_3\text{Si}(\text{OMe}) > \text{Ph}_2\text{Si}(\text{OMe})_2 > \text{PhSi}(\text{OMe})_3$. The results indicate that the structure of phenyl-substituted methoxysilane has a considerable effect on the activity and stereospecificity of the catalyst through activation and/or deactivation of titanium sites. These processes depend on the stereoelectronic characteristics of the Lewis base, the interaction of Lewis base-triethylaluminum, and the catalyst-cocatalyst interactions [29-33].

Influence of Polymerization Parameters

The $\text{MgTi-B}/\text{Et}_3\text{Al} + \text{Ph}_2\text{Si}(\text{OMe})_2$ catalyst system was used to study the effect of polymerization time, temperature, and hydrogen concentration on the efficiency of the catalyst and polymer characteristics.

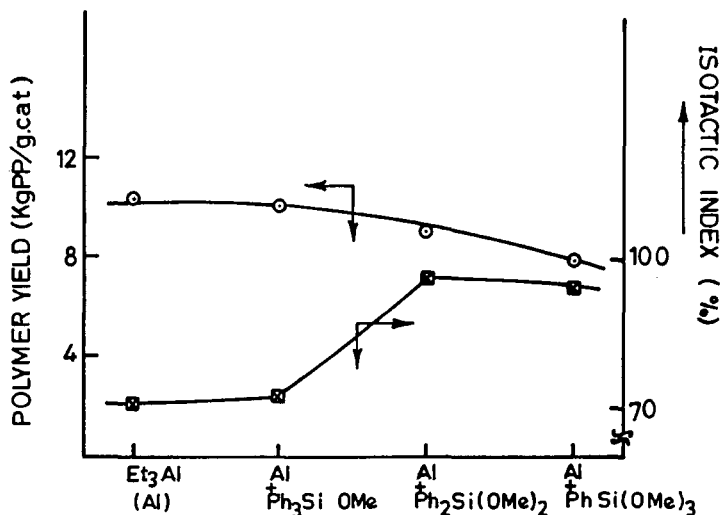


FIG. 2. Polymer yield and isotactic index vs external Lewis base. Catalyst, MgTi-B, 30 ± 2 mg; cocatalyst, Et₃Al, 5 mmol; external Lewis base, 0.25 mmol; $P_c = 7.0 \pm 0.1$ kg/cm²; H₂ = 400 ± 10 mL; time = 2 hours; hexane = 1000 mL; temperature = 70°C.

Evaluation of the performance of the catalyst system as a function of time shows (Fig. 4) an increase of polymer yield with increasing reaction time. The polymer yield is significantly high in the first hour compared to the second hour, indicating a reduction in the average polymerization rate. The isotactic index of polypropylene is not changed appreciably with time due to a proportionate increase in isotactic and atactic polypropylene yield. These observations can be explained on the basis that there is no variation in the activity ratio of isotactic and atactic titanium sites with time.

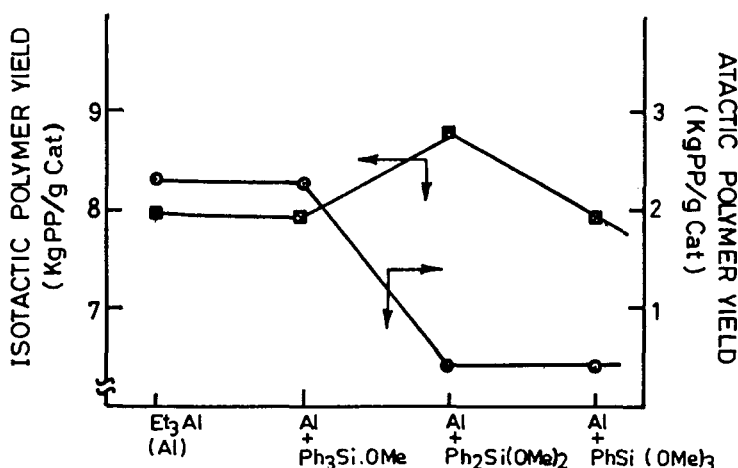


FIG. 3. Isotactic and atactic polymer vs external Lewis base. Reaction conditions as in Fig. 2.

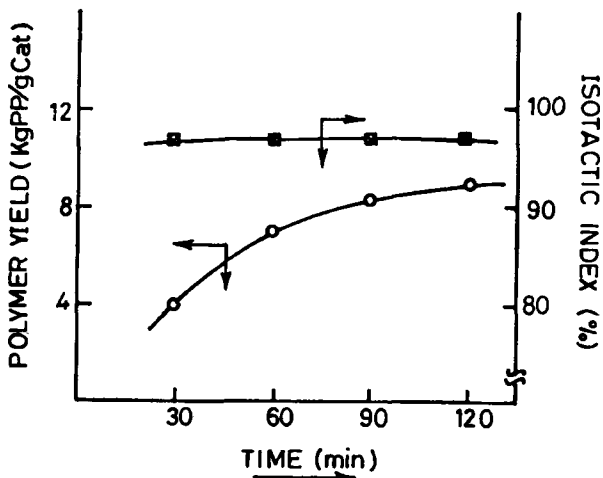


FIG. 4. Polymer yield and isotactic index vs time. Catalyst system: MgTi-B/Et₃Al + Ph₂Si(OMe)₂. Conditions as in Fig. 2 except for time.

The effects of polymerization temperature on polymer yield and the isotactic index are shown in Fig. 5. The results indicate that an increase of temperature from 50 to 70°C enhances the polymer yield by approximately 19% with a reduction (< 1%) in the isotactic index. A further increase of temperature to 90°C brings a drastic reduction (approximately 48%) in polymer yield and a decrease in the isotactic index by 1%. This can be attributed to the irreversible destruction of active titanium centers at 90°C. The melt flow index of the polypropylene obtained is found to change with the variation of temperature (Fig. 6). A twofold increase of MFI is noted with a change

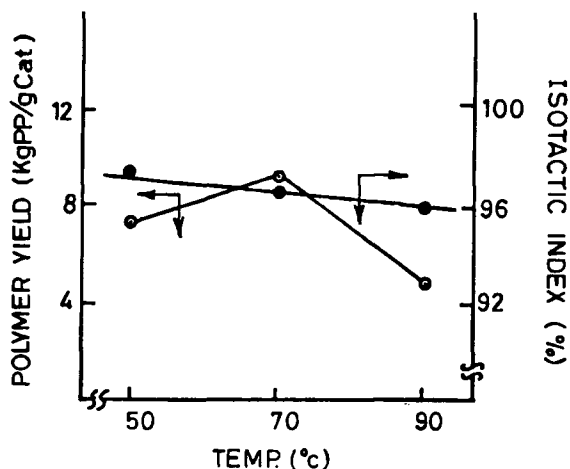


FIG. 5. Polymer yield and isotactic index vs temperature. Reaction conditions as in Fig. 2 except for temperature. External Lewis base: Ph₂Si(OMe)₂.

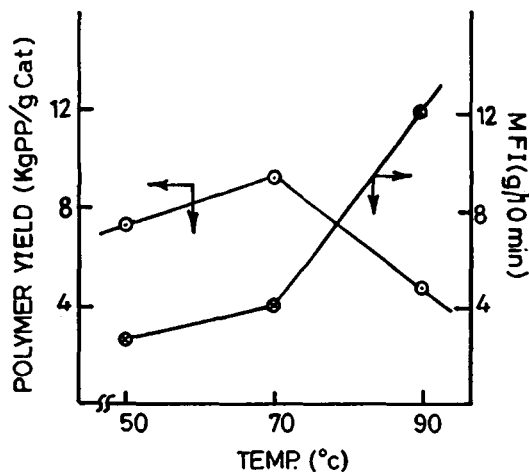


FIG. 6. Polymer yield and melt flow index vs temperature. Reaction conditions as in Fig. 2 except for temperature. External Lewis base: $\text{Ph}_2\text{Si}(\text{OMe})_2$.

of temperature from 50 to 70°C, while a threefold increase is observed with a rise of temperature from 70 to 90°C. These results may be ascribed to an increase in the rate of chain transfer reaction with the rise of temperature, resulting in the formation of lower molecular weight polymers. The overall data indicate that a change of temperature influences the stability of active species, the monomer concentration in the liquid phase, and the chain transfer processes of the polymerization system. These behaviors are reflected in the polymer yield, the isotactic index, and the MFI of polypropylene.

The hydrogen used as a chain transfer reagent in the polymerization reaction influences the polymer yield, the isotactic index, and the MFI (Fig. 7). The increase of hydrogen concentration leads to higher production of polymer with a high MFI value. The GPC data of polypropylene also indicate that \bar{M}_w and \bar{M}_n decrease with an increase of hydrogen concentration [volume of $\text{H}_2 = 150 \text{ mL}$; $\bar{M}_w \times 10^{-5} = 3.0$, $\bar{M}_n \times 10^{-5} = 1.0$, $\bar{M}_w/\bar{M}_n = 3.0$; volume of $\text{H}_2 = 400 \text{ mL}$; $\bar{M}_w \times 10^{-5} = 2.3$, $\bar{M}_n \times 10^{-5} = 1.7$, $\bar{M}_w/\bar{M}_n = 3.2$] with little effect on the molecular weight distribution. The isotactic index of polypropylenes does not change at lower levels of hydrogen (< 250 mL), indicating an equal increase in the activity for both isotactic and atactic sites of the catalyst system. At higher hydrogen concentrations (> 250 mL) the reduction in the isotactic index is due to a relatively larger increase in the yield of the heptane-soluble fraction (atactic) of polypropylene (Fig. 8). The improvement in activity with the addition of hydrogen may be attributed [34, 35] to the formation of Ti^{3+} active sites from inactive Ti^{2+} species through oxidative addition. Some of the Ti^{3+} species that becomes deactivated during polymerization can be regenerated by hydrogenolysis [34]. The other factors responsible for improvement in the polymer yield may be the higher rate of migration of polymer chains for active centers and the reduction of double-bond-terminated polymer chains with an increase of hydrogen concentration [36].

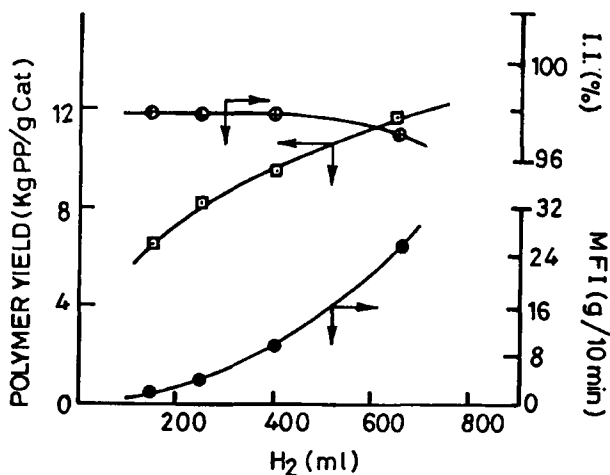


FIG. 7. Polymer yield, isotactic index, and melt flow index vs hydrogen concentration. Reaction conditions as in Fig. 2 except for the amount of hydrogen. External Lewis base: $\text{Ph}_2\text{Si}(\text{OMe})_2$.

Polymer Morphology

The activity and texture of the catalyst is known to affect the polymer morphology because polymer particles replicate the morphology of catalyst particles [37]. The SEM study of polypropylene particles obtained with the $\text{MgTi-B}/\text{Et}_3\text{Al} + \text{Ph}_2\text{Si}(\text{OMe})_2$ system shows (Fig. 9) a nonspherical shape of the polymer particles.

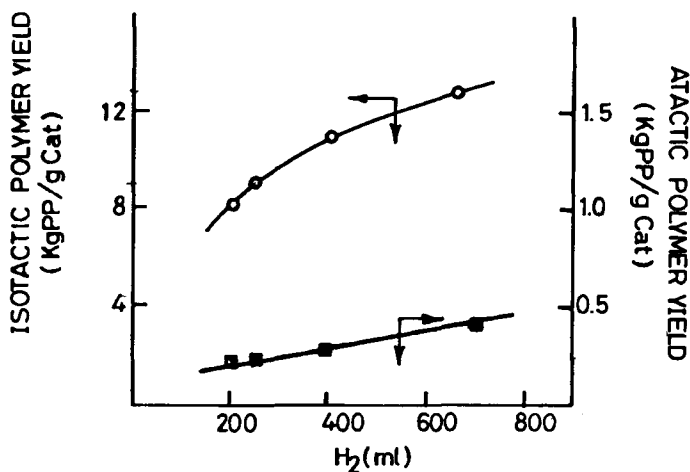
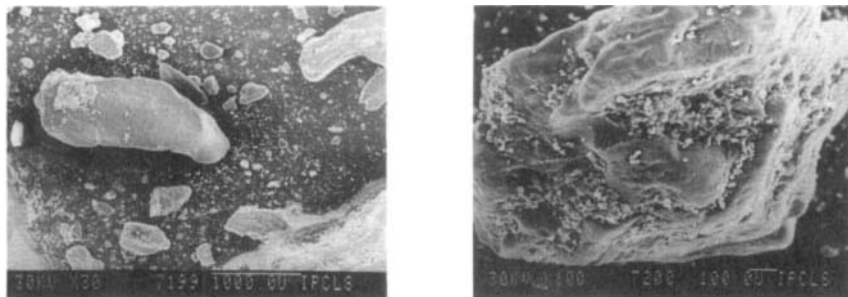


FIG. 8. Isotactic and atactic polymer yield vs hydrogen concentration. Reaction conditions as in Fig. 2 except for the amount of hydrogen. External Lewis base: $\text{Ph}_2\text{Si}(\text{OMe})_2$.



(A)

(B)

FIG. 9. SEM of polymer particles. (A) 30 \times magnification. (B) 100 \times magnification. Polymerization conditions as in Table 1. Catalyst: MgTi-B.

CONCLUSIONS

The following conclusions are drawn from the results obtained in the present investigation.

1. The preparation of supported titanium catalysts involving the in-situ generation of MgCl_2 from magnesium ethoxide and the incorporation of TiCl_4 and dibutyl phthalate give high efficiency catalyst systems for propylene polymerization.

2. The incorporation of dibutyl phthalate as an internal Lewis base in the solid catalyst improves the productivity of the catalyst system through the generation of highly active and stereospecific titanium sites. The amount of dibutyl phthalate in the solid catalyst determines the efficiency of the system.

3. The number of methoxy groups present in phenyl-substituted methoxysilanes, used as external Lewis bases in conjunction with Et_3Al , influences the yield and isotactic pattern of the catalyst system. The efficiency of external Lewis bases studied at a fixed triethylaluminum-to-silane ratio decreases in the order $\text{Ph}_2\text{Si}(\text{OMe})_2 > \text{PhSi}(\text{OMe})_3 > \text{Ph}_3\text{Si}(\text{OMe})$.

4. The stability of titanium species, the activities of isotactic and atactic sites, chain transfer processes and/or monomer concentrations, etc. are contributing factors in the variation of the performance of catalysts. These variations are linked with such polymerization parameters as time, temperature, and hydrogen concentration.

5. The polypropylene particles are nonspherical.

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